

Sorbent Bed Acquisition and Compression of Carbon Dioxide from the Mars Atmosphere

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ABSTRACT

Human exploration of Mars as well as unmanned sample return missions from Mars can benefit greatly from the use of propellants produced from the resources available from the atmosphere of Mars. The first major step of any in-situ propellant production (ISPP) system is to acquire carbon dioxide (CO₂) from the Mars atmosphere and compress it for further chemical processing. One system that performs this step is called a Mars Atmosphere Acquisition and Compression (MAAC) unit. A simple prototype MAAC was developed by JPL as part of the Mars ISPP Precursor (MIP) experiment package for inclusion on the Mars 2001 Surveyor Lander. The MAAC consists of a valved enclosure packed with a sorbent material which selectively adsorbs CO₂ from the Mars atmosphere (valves open), desorbs and compresses the acquired CO₂ by heating (valves closed) and then delivers the pressurized CO₂ to an oxygen generating system where the CO₂ is electrolyzed to produce oxygen. This paper presents a description of the MAAC experiment, the several iterations involved in arriving at the MAAC design, and the results of MAAC performance testing.

INTRODUCTION

Returning surface material samples from Mars has been a topic of prime interest to many contemporary Mars mission scientists and architects. Further, in recent years there has been considerable serious discussion about the plausibility of human exploration of Mars. It has been generally recognized that a primary enabling factor for either a large sample return mission or human exploration is the ability to produce propellants from the natural resources available from the Martian atmosphere. The composition of the Martian atmosphere was analyzed by the Viking mission in 1976 and found to consist of a mixture of ~95% CO₂, ~3% N₂, and ~2% Ar (vol %). Shortly thereafter, in 1978, Ash, Dowler, and Varsi [1] proposed the electrolytic decomposition of CO₂ into CO and O₂ to produce and collect O₂ propellant. This process, along with other processes proposed subsequently, are categorized under the rubric In-Situ Propellant Production (ISPP), which in

turn is regarded as a subset of the larger category In-Situ Resource Utilization (ISRU).

Before CO₂ can be electrolytically decomposed, it must first be separated selectively from the Martian environment (so that the product O₂ purity will be high) and then pressurized to a high enough level to enable sufficient throughput to a reactor. Reactors functioning at Mars pressure (~ 6 torr) would require very high volumetric flow rates. A standard mechanical compressor is far too heavy and bulky to be considered for such service. However, an adsorption-based compressor system employing the steps: 1) adsorb CO₂ from the atmosphere in an open sorbent-filled container at a cold temperature, 2) close the container at the end of the sorption period, and 3) desorb CO₂ by heating the CO₂-rich sorbent in a closed container, can deliver pressurized CO₂ in a mass-efficient manner.

In 1997, JPL began the design and development of such a sorption compressor, the Mars Atmosphere Acquisition and Compression (MAAC) experiment, as part of the Mars ISPP Precursor (MIP) development project. MIP is an integrated five-experiment package that was designed to be included as one of the payloads on the deck of the Mars 2001 Surveyor Lander. This paper will discuss the details of the development effort of MAAC from conceptual design to fabrication of flight hardware. We will describe our design failures as well as successes, our laboratory test results, and a brief statement about future designs of MAAC-like equipment.

MAAC DEVELOPMENT UNIT DESIGN

A cyclic adsorption process involves the selective adsorption of a specific constituent on the surface of a sorbent material at a condition favorable to adsorption (typically at a cold temperature) followed by the subsequent desorption of that constituent at a condition less favorable to adsorption (typically at a higher temperature and sometimes at a lower pressure). Industrial adsorb/desorb processes typically involve flowing pressurized feed gas into an adsorption tower where a selected constituent (typically a contaminant) is removed from the gas stream by adsorption. Adsorption continues until

"breakthrough" of the adsorbed constituent occurs at the exit of the adsorption bed at which time the feed gas is rerouted into a parallel, freshly desorbed bed. The "CO₂-rich" adsorption bed is then "regenerated" by heating to desorb the previously adsorbed constituent. The desorbed gas is typically fed to another system for further processing or disposal. Finally, the regenerated bed is cooled and held at a standby condition until it is needed to begin a new cycle.

As an initial design concept for MAAC, a variant of this "standard" adsorption/desorption process was studied. It might be thought that adsorption of Martian CO₂ could be effected by simply exposing a suitable bed of sorbent through an opening to the Mars atmosphere and, as CO₂ gets adsorbed on the sorbent creating a local vacuum, further flow of Martian CO₂ would be induced into the sorbent bed, provided that the pressure drop in the opening does not exceed the local vacuum at the sorbent. However, Clark, et. al. [2] under contract with JPL, had previously shown that the lesser adsorbed gases Ar and N₂ will quickly build up inside the sorbent bed forming a "diffusion barrier" which significantly impedes the CO₂ adsorption rate. Since the capacity of a typical sorbent for CO₂ is high (on the order of 0.2 g CO₂ per g sorbent), high partial pressures of unadsorbed Ar and N₂ can build up quickly in the connecting lines and the sorbent bed as the adsorption process proceeds. To thwart this Ar and N₂ buildup, the first MAAC concept employed a fan/blower to feed fresh Mars atmospheric gas by forced draft into the sorption bed, and to blow out residual Ar + N₂ from the bed in the process. Using such a forced draft system for blowing a simulated Mars atmospheric mix (Mars-mix) into a sorbent bed, the CO₂ adsorption capacity yield was adequate, albeit lower than would be predicted using CO₂ adsorption isotherm data from the literature. However, this concept was quickly discarded since the mass, power and volume needed for the fan did not fit within the resource allocations available for the MAAC experiment. Therefore, it was decided that MAAC would operate by relying only on diffusion of fresh CO₂ from the Mars atmosphere into the sorbent bed.

In order to rely only on diffusion, a scheme to overcome the diffusion barrier created by unadsorbed trace gases (mainly N₂ and Ar) needed to be developed. The MAAC development team proposed to apply an occasional backflow of pure, pressurized CO₂ to periodically flush out residual Ar and N₂ back through the Mars-mix feed valve. It was calculated that by collecting about 3% of the predicted daily production of pressurized CO₂ in a "purge tank" during the desorb process, three sorbent bed volume equivalents of CO₂ could be back-flushed through the bed once every 15 minutes during the 16 hour overnight adsorption period. It was hypothesized that this "backflow" process would flush out the residual Ar and N₂ back through the Mars-mix feed valve into the Mars atmosphere (assuming that the purge CO₂ did not quickly get readsorbed) and subsequently allow

fresh CO₂-rich Mars mix to enter the sorbent bed, thus enhancing the CO₂ sorption rate. This became the initial development unit baseline concept for the MAAC.

The MAAC team faced another design challenge besides the CO₂ adsorption capacity/rate problem caused by unadsorbed trace gases. Since the sorbent capacity for CO₂ increases as the temperature decreases, there is significant incentive to cool the sorbent bed as quickly as possible after the end of the desorb heating process. However, there is also a significant incentive to keep the sorbent bed well insulated to minimize heat loss (and power consumption) during the desorb heating process. To resolve this dichotomy, a novel gas-gap heat switch was devised by J. Wu at JPL (see Figure 1). This heat switch would be turned off during the desorb process to conserve heat, but would be turned on during the adsorb process to conduct heat away from the bed to a radiator directed towards the Mars night sky. The gas-gap heat switch operated on the principle that when the switch is on, pressurized hydrogen gas will conduct heat from an outer copper cup to an inner copper cylinder across a gap of 0.13 mm. To turn the switch off, the hydrogen is adsorbed onto a hydrogen-selective adsorbent material leaving a vacuum in the gap between the cup and the cylinder. To turn the switch back on, a 1 W heater would be enough to desorb the hydrogen from the sorbent and allow it to flow back into the gap to once again conduct heat across the gap. Figure 2 shows an illustration of the development unit MAAC sorbent bed with the heat switch. Figure 3 is a schematic of the overall MAAC development unit system.

MAAC DEVELOPMENT UNIT TESTING

Pre-delivery testing of the MAAC development unit was conducted in September 1998 in a vacuum chamber conditioned with a simulated Mars-mix environment at 6 torr. These tests demonstrated a MAAC CO₂ adsorption capacity of about 0.03 g CO₂ adsorbed per gram of sorbent after 16 hours of adsorption, even though "backflow" purging with high pressure CO₂ was employed. This yield was far below the saturation value of ~ 0.2 g/g that we subsequently measured (see Table 1). This result indicated that the purge system did not work the way we had hoped it might. A different approach was needed.

SORBENT ADSORPTION RATE AND CAPACITY CHARACTERIZATION TESTING

In February 1999, a laboratory test set-up was devised to measure the specific adsorption rate of CO₂ on a variety of sorbents at a variety of gaseous compositions at constant temperature. In this laboratory configuration, the test setup ensured that the sorbent was always exposed to the appropriate gas without any diffusion impediment. Results from these tests are given in Table 1. From these results, it was determined that CO₂ adsorption occurred rapidly and that the gas/solid phase equilibrium for CO₂ was

established very quickly no matter what sorbent was used. We further determined that the rate of adsorption of CO₂ onto the sorbent was strictly limited by the rate at which fresh CO₂ could diffuse into the bed. The choice of the optimum sorbent is made on the basis that we desire the highest capacity from a cycle where adsorption takes place at low T and P, and desorption takes place at high T and P. A secondary consideration is that it is desirable that the sorbent release its CO₂ at a minimum high temperature in the desorption step. The Zeolite 5A is clearly inferior in performance with respect to these criteria. However, the carbon molecular sieve (CMS) and Zeolite 13X are more competitive. Around a cycle from (T=-79°C, P = 6 torr) to (T=177°C, P = 700 torr), the Zeolite 13X provides 17.6 g CO₂/g sorbent, whereas the CMS provides only about 15.3 g CO₂/g sorbent. The 13X has a slightly superior capacity. In addition, the 13X continues to adsorb well at -79°C if the pressure is lower than 6 torr, whereas the performance of the CMS falls off. Since the Mars surface pressure is variable with location and season, this is an advantage for the Zeolite. An advantage of the CMS is that it releases its CO₂ at lower temperatures than the Zeolite. Nevertheless, it was concluded that the sorbent Zeolite 13X is the best compromise as the sorbent of choice for MAAC. If the CMS can be modified to increase its capacity, the advantage of lower temperature release of CO₂ might make it a superior choice for future applications.

Because the sorbent characterization tests yielded adsorption capacity values much higher than were measured during tests of the initial MAAC development unit design, it became very clear that the purge system did not work. It was concluded that, in order to improve the overall CO₂ adsorption rate, a more efficient design was required that would provide both an increase in the cross sectional area and a decrease in the length of the CO₂ diffusion path from the atmosphere to the sorbent bed. Further, it was clear that if these changes in design (substantial increase to the cross-sectional area and decrease to the diffusion path length) could not be implemented because of MIP interface constraints, a much longer adsorption time than 16 hours would be needed to collect the quantity of CO₂ needed for the OGS experiment. During the summer of 1999, several design options were explored including one that used a vacuum-rated butterfly valve as the primary MAAC interface with the Martian atmosphere (see Figure 4). This design provided the needed large opening (1.87"; 47.5 mm) and a short diffusion length (< 4"; ~100 mm) but confidence in the design waned quickly because of skepticism regarding whether or not the valve seal would survive the open/close cycling operations without leaks. Nonetheless, this design was used to test the validity of the MAAC adsorption concept and yielded very useful data which clearly indicated that indeed if the opening to the environment was large enough, the sorbent could easily saturate with CO₂ within the allotted 16-hr

overnight period. This test data is presented in Table 2.

Larger solenoid valves were also considered but the same potential valve seal failure concern quenched these ideas as well. It was finally decided that, since by now, flight valves having an orifice diameter of 0.085-in (2.16 mm) had been specified, purchased and leak-qualified for this service at considerable cost, it was necessary to find a way to use these valves in the modified MAAC design. Also, the option of making significant changes to the MAAC configuration had long passed.

It was finally concluded that the practicalities of the MAAC development (mass, volume, funding, schedule) precluded implementation of a system with a substantial increase to the cross-sectional area and decrease to the diffusion path length. However, the test results showed that a 64-hour adsorb time would be sufficient for a small tube to collect enough carbon dioxide to meet the demand of the Oxygen Generating Subsystem (OGS) operations. From this finding, it was determined that the heat switch/radiator cooling system was no longer needed to cool down the sorbent since the bed would cool by itself within this longer adsorb period. Therefore, the heat switch and the radiator were dropped from the MAAC Qualification Unit design.

MAAC QUALIFICATION UNIT DESIGN

By September 1999, a new MAAC design was presented to and accepted by the MIP project management. This revised MAAC configuration is shown in Figure 5 and was the design presented at the Critical Design Review. An increased cross-sectional area for CO₂ diffusion was accomplished by opening up the main entrance into the MAAC sorbent bed, and increasing the line size of the feed tube from 1/8" (6.35 mm) to 1" (25.4 mm). A stainless steel bellows was added in-line to provide a tortuous path for heat flow in order to minimize heat-loss from the MAAC sorbent bed through the feed tube during desorption. The effective valve opening cross-sectional area was doubled in the new configuration by using two Mars atmosphere isolation valves with 0.08" openings. Because the purge system concept had been abandoned after laboratory tests conducted in April 99 had proven it was totally ineffective, the purge valve was available for use as one of the Mars atmosphere isolation valves.

Fabrication of the MAAC qualification unit was expedited and by late October 1999, the new MAAC was ready to be tested. It was decided to allow a period of 64 hours (16 + 48 hours; 1 night and 2 full days) for the MAAC adsorption phase. With this timing, the MAAC could deliver CO₂ to the OGS about twice per week. The integrated MIP MAAC/OGS Configuration is shown in Figure 6. The MAAC qualification unit was delivered to Johnson Space Center in mid-November 1999.

MAAC QUALIFICATION UNIT TESTING

The integrated MIP qualification unit was subjected to a pre-qualification thermal vacuum test in mid-January 2000 during which the MAAC was subjected to a Mars-mix atmosphere and performed very well. The test results indicated that MAAC made enough CO₂ for the OGS unit to make oxygen as planned.

In early February 2000, the integrated MIP qualification unit was subjected to the vibration qualification testing. A post-vibration test leak check of the MAAC hardware revealed a large leak had developed in the bellows. Further, some of the thermal insulation had been pulverized and had worked its way out of the MAAC insulation containment can and into the MIP package enclosure.

Both of these problems were cause for further MAAC re-design. However, available funding for the MAAC instrument development had been exhausted and the MAAC project was halted. In late March 2000, after considerable review of the two recent Mars mission failures (Mars Climate Orbiter and Mars Polar Lander), NASA headquarters management made the decision to cancel the Mars 2001 Surveyor Lander mission pending further mission architecture planning and design investigation. However, it was decided that the fabrication and testing of the Mars 2001 Surveyor Lander's flight experiments should be completed so that they could be included on a later Mars mission, perhaps the 2003 Mars Lander.

MAAC FLIGHT UNIT DESIGN AND PLANNED TESTING

With a new funding commitment at the beginning of April 2000, the MAAC re-design effort resumed. Figure 7 illustrates the final MAAC Flight Unit design of the MIP/MAAC experiment. The bellows leak was determined to have been caused by metal-to-metal contact of the containment can with the bellows during the vibration test. Therefore, design changes were made to the insulation containment can so that there could be no metal-to-metal contact between the containment can structure and the bellows. The insulation length was reduced on both ends to provide for less stress on the bellows due to compression during installation. Multilayer insulation was added to cover the bellows to minimize the added heat loss resulting from the new design changes. Several structural improvements were included to lower the resonant frequency of the MAAC assembly and thus limit its movement latitude during vibration testing. The sorbent bed mounting structure stiffness was increased to minimize flexure during high vibration loads. The valve assembly plate was tied to the sorbent bed mounting structure with a bracket so that the MAAC assembly could be delivered and mounted onto MIP as one structural unit instead of two.

The MAAC flight hardware design is now essentially complete. The current plan is to modify the MAAC

Qualification Unit in May 2000 to match this design. The MAAC Qualification Unit then will be shipped to JSC for fit check on the MIP structure and for a repeat of the qualification vibration testing. Fabrication of the MAAC Flight Unit is planned for May/June 2000. Upon completion of fabrication, the MAAC Flight Unit will be tested in a simulated Mars environment. After testing, the hardware will be delivered to JSC for integration onto the MIP Flight Unit structure.

FUTURE MAAC DESIGNS

There were several important lessons learned from the MAAC development experience. First, if the MAAC sorbent material is to reach saturation with CO₂ within a 16-hour adsorb period, the bed must be effectively exposed to fresh Mars atmosphere during the entire adsorption process. This exposure can be accomplished either by providing a much larger opening to the bed so that CO₂ diffusion is not impeded and unadsorbed Ar and N₂ can quickly diffuse away, or by providing an induced draft fan to draw unadsorbed Ar and N₂ from the bed allowing fresh CO₂-rich Mars atmosphere to flow into the bed. Several such improved MAAC designs have been proposed and may be included on future Mars Lander missions. Design details for these improved MAACs are not yet available for publication.

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The authors wish to thank NASA for supporting this research and development work. We specifically thank the MIP Principal Investigator, David Kaplan, for his efforts in providing the opportunity for JPL to perform this interesting work. The production of propellant from in-situ resources is an intriguing idea and the MIP experiments hopefully will yield the first demonstration of chemical processing of in-situ resources on another planet. We feel that the entire MIP team has learned much about the physical mechanisms governing CO₂ adsorption from the Mars atmosphere during this MAAC development effort. We particularly want to recognize the efforts of Howard Flynn and Phil Cota at the Johnson Space Center (JSC) for conducting a parallel set of adsorption tests during the summer of 1999 which yielded data that correlated well with the JPL data. These JSC tests helped lead us to a final design configuration and operating scenario for MAAC. We also wish to thank Dr. John Finn at the NASA Ames Research Center for suggesting improvements to the MAAC configuration. Finally, we want to acknowledge the important contributions of Dr. Pramod Sharma who conducted the sorbent characterization testing. Dr. Sharma died of a

massive stroke in September 1999 shortly after completing this important work.

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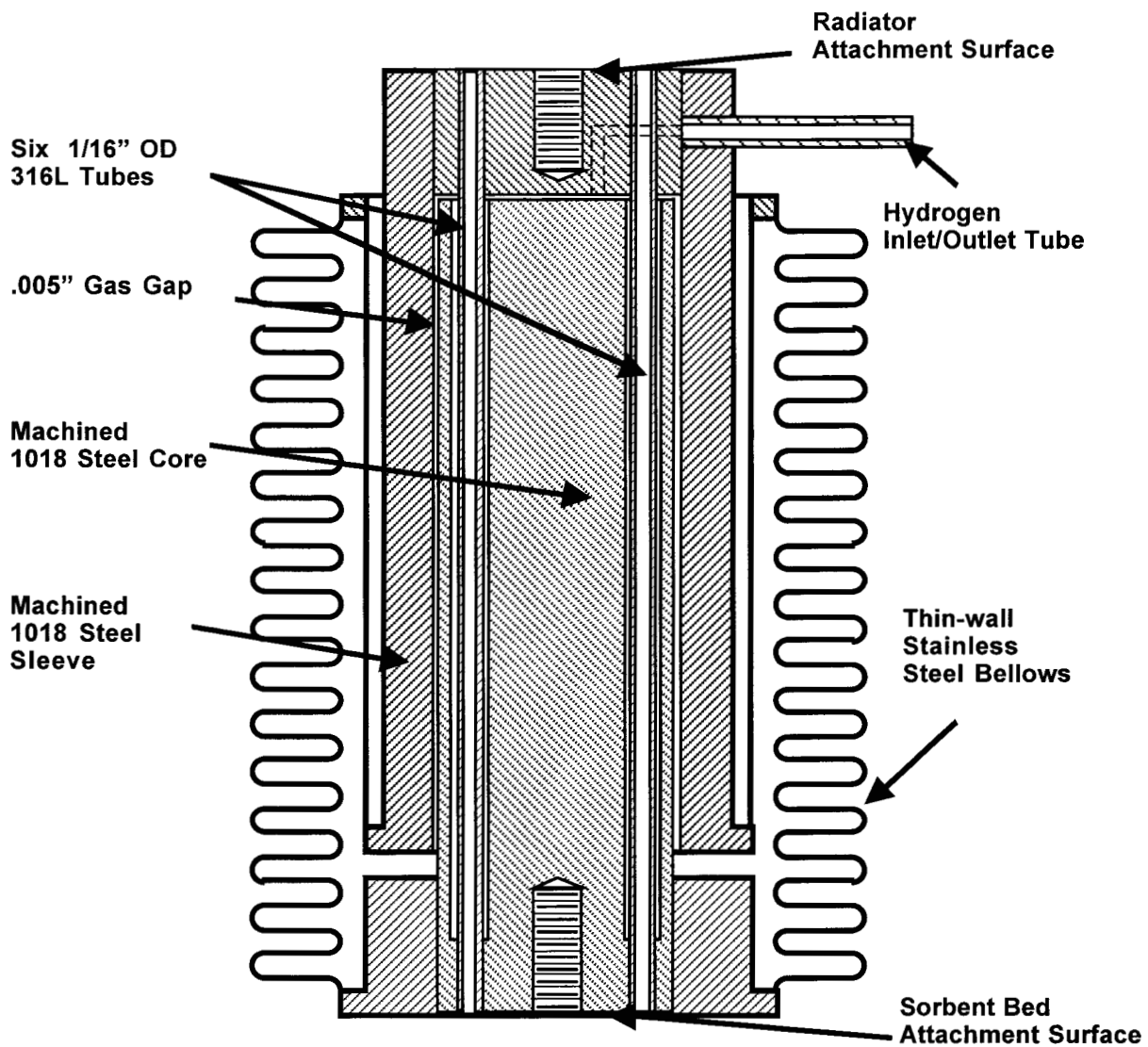


Figure 1. Gas-gap Heat Switch Conceptual Drawing

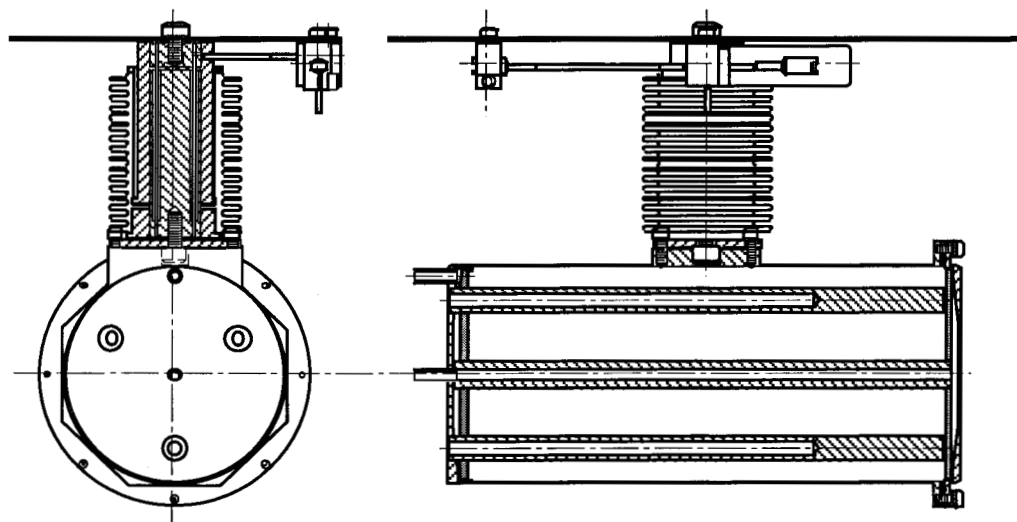


Figure 2. MAAC Sorbent Bed Assembly (May 1998)

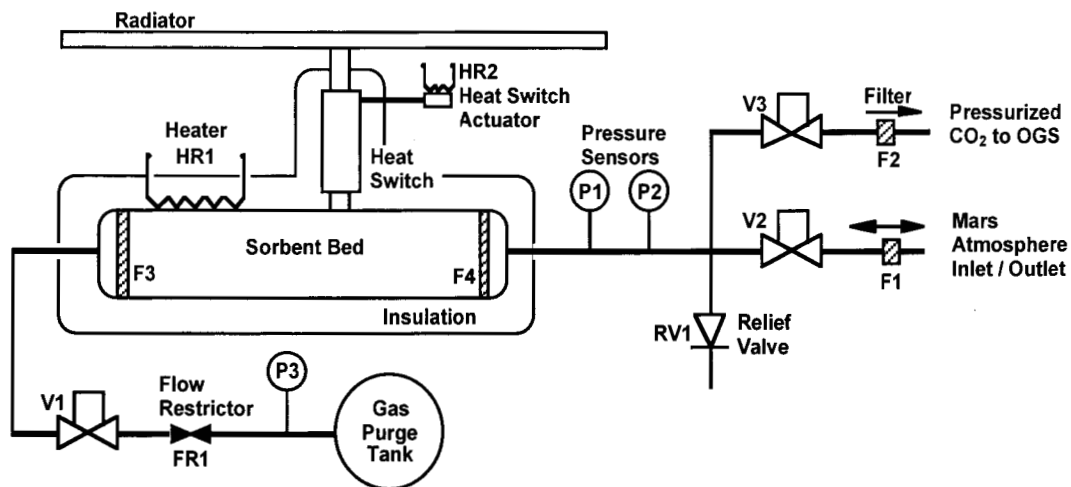


Figure 3. MAAC System Schematic (May 1998)

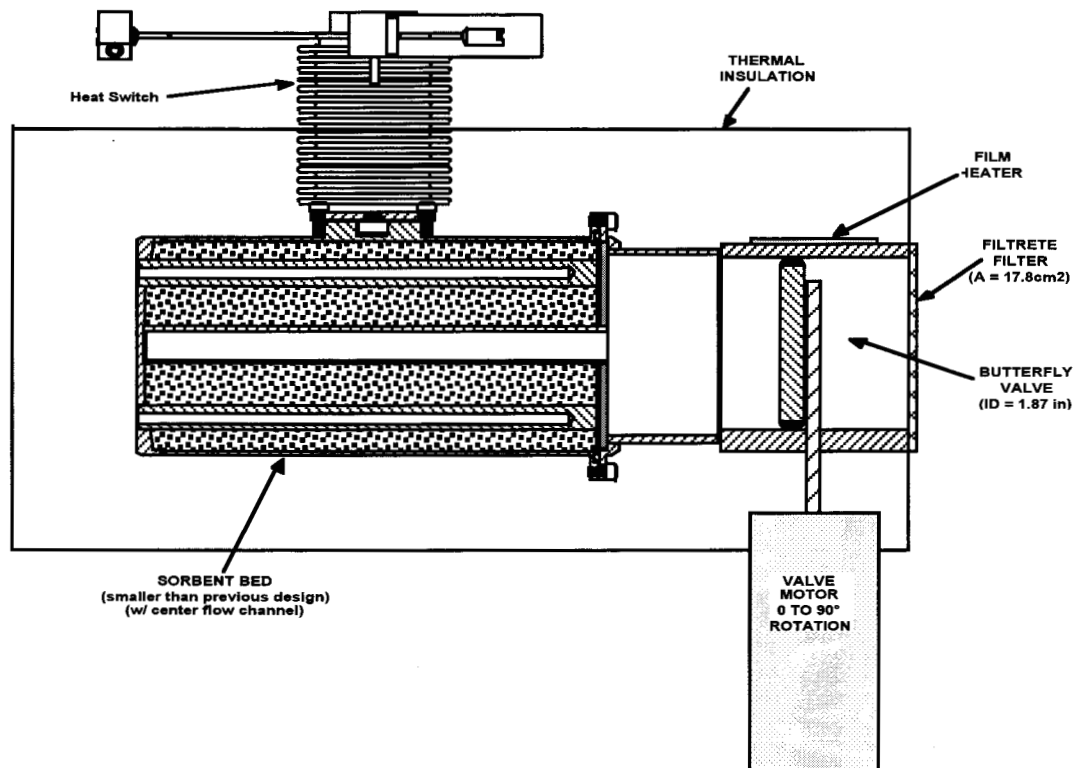


Figure 4. Alternative MAAC concept with Butterfly Valve Opening

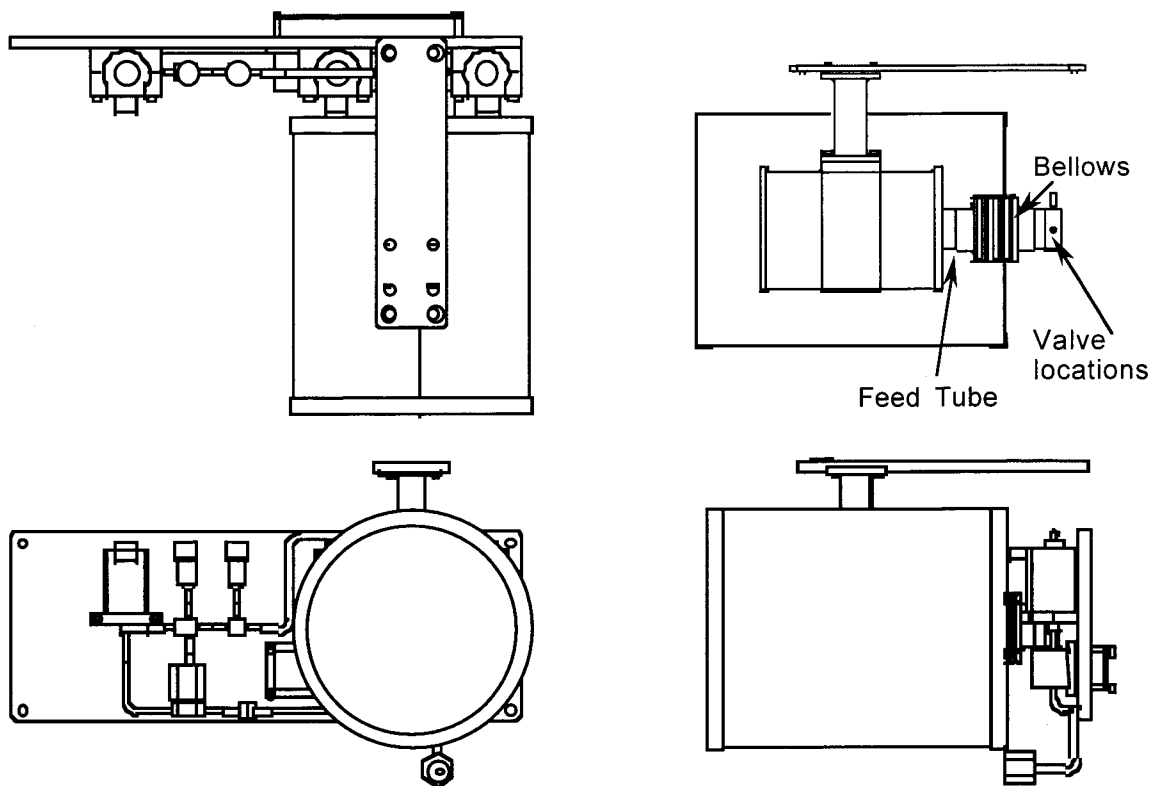


Figure 5. The MAAC Qualification Unit Configuration

Integrated MIP MAAC/OGS Configuration

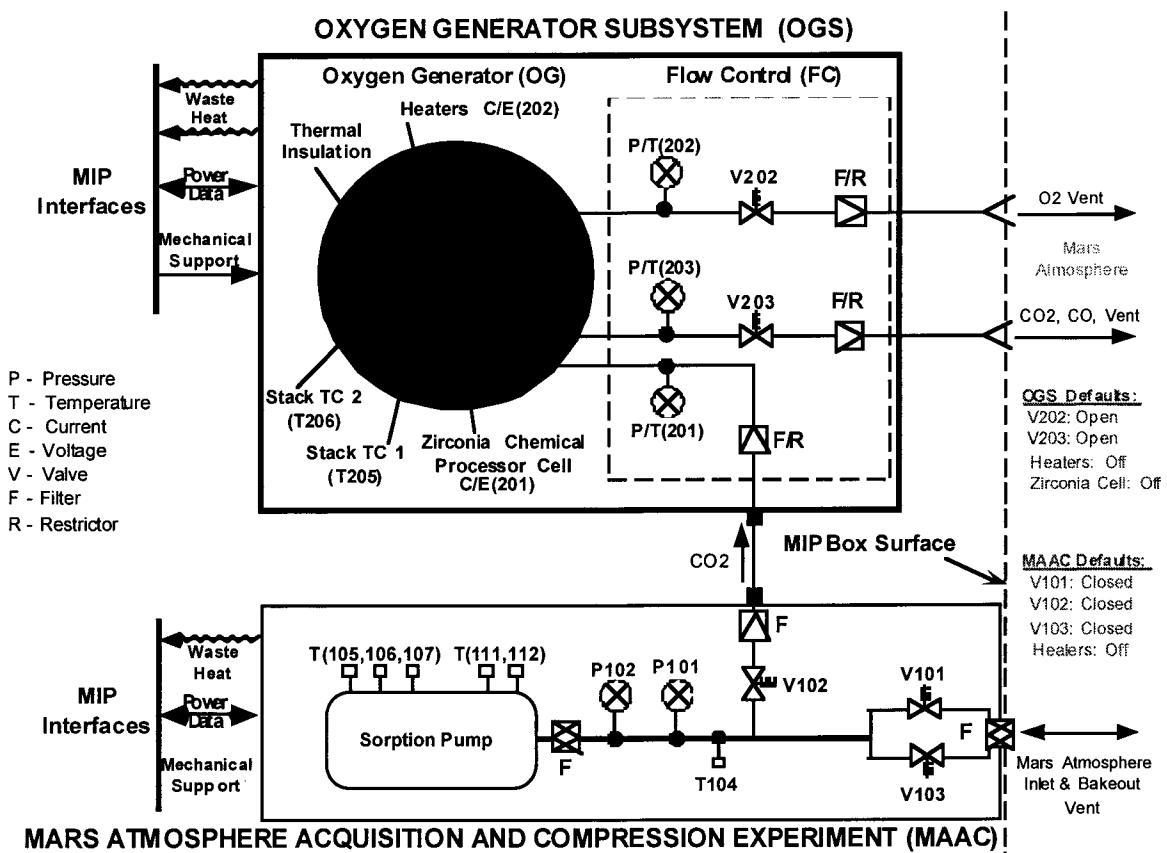


Figure 6. Integrated MIP MAAC/OGS Configuration

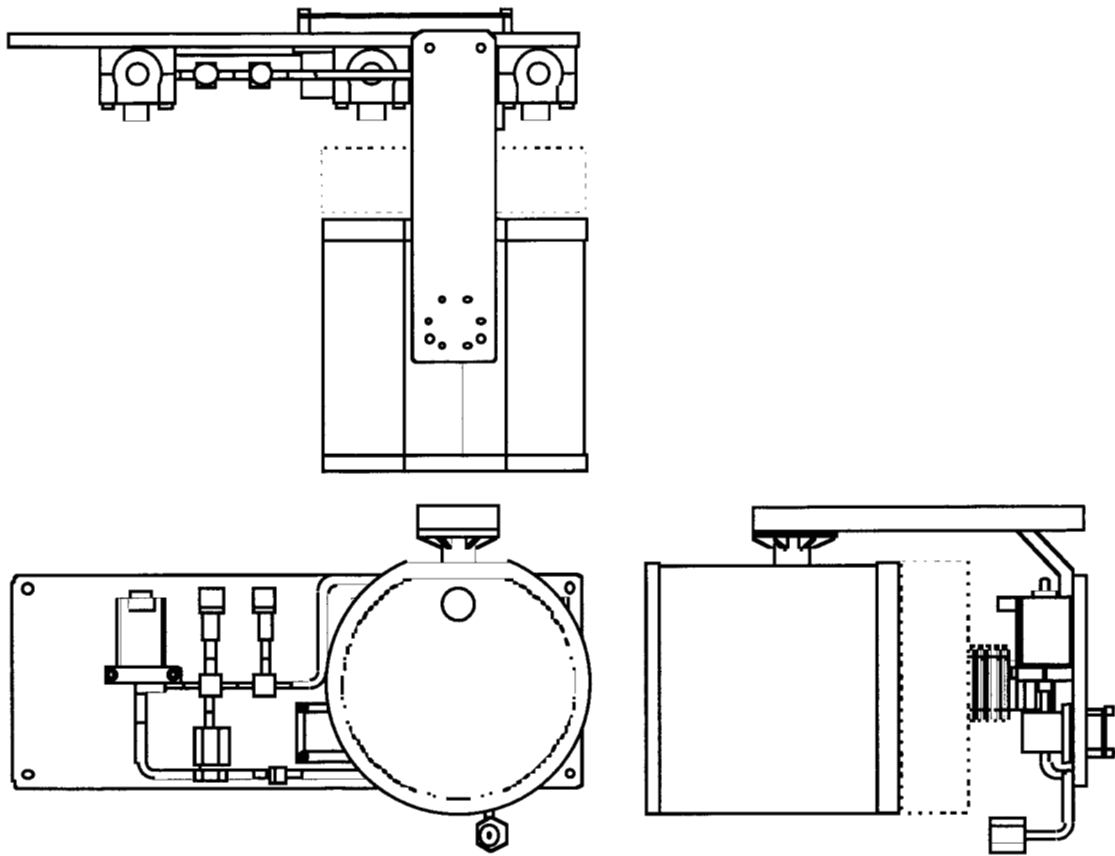


Figure 7. MAAC Flight Unit Configuration (April 2000)

Table 1. CO2 Adsorption Measurements for Three Sorbent Materials
1) Carbon Molecular Sieve, 2) 13X Zeolite, 3) 5A Zeolite

JPL ADSORPTION MEASUREMENTS USING KAHN MICROBALANCE						
Sorbent Material	Temperature (C)	CO2 Partial Pressure (torr)	N2 Partial Pressure (torr)	Ar Partial Pressure (torr)	Total Pressure (torr)	Quantity Adsorbed (wt%)
CMS	-79	0.2			0.2	2.88
CMS	-79	1.0			1	7.12
CMS	-79	3.0			3	12.4
CMS	-79	6.0			6	18.6
CMS	-79	6.0			6	17.6
CMS	-79	6.0			6	17.06
CMS	-79	10.0			10	21.2
CMS	-79		1.0		1	0.16
CMS	-79	5.0	1.0		6	16.87
CMS	-79		6.0		6	0.64
CMS	-79			6.0	6	0.636
CMS	-79	6.0		6.0	12	17.4
CMS	-79	5.7	0.18	0.12	6	16.75
CMS	0	6.0			6	1.12
CMS	0	700.0			700	22.62
CMS	100	6.0			6	0
CMS	100	700.0			700	6.08
CMS	177	6.0			6	0
CMS	177	700.0			700	2.22
13X	-79	0.2			0.2	16.18
13X	-79	1.0			1	21.18
13X	-79	3.0			3	23.2
13X	-79	6.0			6	24.28
13X	-79	10.0			10	25.2
13X	-79		6.0		6	0.097
13X	-79	6.0	6.0		12	23.5
13X	0	6.0			6	9.32
13X	0	700.0			700	22.2
13X	100	6.0			6	0.886
13X	100	700.0			700	12.85
13X	177	6.0			6	0.167
13X	177	700.0			700	6.65
5A	-79	0.2			0.2	14.13
5A	-79	1.0			1	16.23
5A	-79	3.0			3	17.26
5A	-79	6.0			6	17.71
5A	-79	10.0			10	18.11
5A	0	6.0			6	9.437
5A	0	700.0			700	17.2
5A	100	6.0			6	0.652
5A	100	700.0			700	12.04
5A	177	6.0			6	0.097
5A	177	700.0			700	5.31

Table 2. Testing to Determine Adsorption Rates with Various Orifice IDs

136g of 13X zeolite
 2.0" ID x 4.5" sorbent bed
 Mars Mix (95% CO2, 3% N2, 2%Ar)
 Max Desorption Temperature 442K
 Nighttime Adsorption Temperature 213K (16hr duration)
 Daytime Adsorption Temperature 248K (8hr duration)

• 1.84" ID Butterfly valve	14hr adsorb	223 torr desorption pressure	23.4g delivered	
• 0.60" ID Butterfly valve	14hr adsorb	600 torr desorption pressure	10.4g delivered	
• 0.60" ID Butterfly valve	20hr adsorb	600 torr desorption pressure	14.0g delivered	
• 0.60" ID Butterfly valve	38hr adsorb	600 torr desorption pressure	26.7g delivered	
• 0.30" ID x 2.0" tube inlet	38hr adsorb	600 torr desorption pressure	6.1g delivered	
• 0.88" ID x 5.0" + filter	38hr adsorb	600 torr desorption pressure	13.8g delivered	
• Dual .080" x 2.0" tubes	64hr adsorb	600 torr desorption pressure	2.7g delivered	
• Dual .080" x 2.0" tubes	64hr adsorb	700 torr desorption pressure	6.1g delivered	(2nd cycle)
• Dual .080" x 2.0" tubes	40hr adsorb	700 torr desorption pressure	4.3g delivered	(3rd cycle)